
JUSTIFICATION OF THE CHOICE OF CATALYST FOR THE OXIDATION OF C3-C4 ALDEHYDES INTO ACIDS AND THEIR MODIFICATION

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ABSTRACT

The catalysts used to oxidize unsaturated aldehydes into the corresponding acids are complex oxide systems. The main component of such oxide systems is molybdenum. Molybdenum itself, without additives, is not used as an independent catalyst. The most widespread use as an additive is phosphorus, which markedly increases the stability of the molybdenum catalyst.

Significantly improve the properties of the catalyst named the presence of vanadium as well, an important role played by such elements as copper, antimony, tungsten, iron, tellurium, and bismuth. The presence of these elements brings the yield of acrylic acid to an average of 95% and methacrylic acid up to 68%. The use of heteropolyacids as oxidation catalysts is advantageous because they possess a particular set of properties necessary for processes in catalysis. The use of heteropolyacids as oxidation catalysts is beneficial because they contain a special set of required properties for processes in catalysis. High thermal stability in the solid-state uses heterogeneous catalysts in oxidation reactions with a wide temperature range. An essential role in the effective use of phosphormolybdenum heteropoly acids is played by their preparation methods, which involve the synthesis based on ammonium salts of phosphorus and molybdenum and on phosphormolybdenum acid. Each series of experiments is represented by samples of catalysts with a wide range. A characteristic point in the formation of the desired catalytic system is the activation of the catalyst. For polycomponent systems, it is difficult to assess the contribution of each introduced component or modify the additive that affects the activity and selectivity of the catalyst. The formation of a two-phase system of zinc molybdate and the ammonium salt of the heteropoly acid appears to be the decisive condition for increasing the activity of the multi-component catalyst when zinc is introduced into its composition. One should pay attention to the number of water molecules in the heteropolyanion sphere and in the channels between them. The catalyst of the proposed composition provides a high yield of the target product.

Keywords: heteropoly acid, acrolein, methacrolein, oxidation, thermal stability.

1. INTRODUCTION

Processes to produce acrylic and methacrylic acids and corresponding aldehydes by gas-phase catalytic oxidation have been developed since the early 1980s [1]. The intensity of development has increased in recent years. The leading countries are Japan and the USA; they account for three-quarters of the filed patents for acrolein and methacrolein oxidation catalysts.

Catalysts for the oxidation of unsaturated aldehydes into acids [2] are complex oxide systems. Molybdenum is a mandatory component in most of them (90%). Individual molybdenum oxide is not used as a catalyst; as a rule, it is used in combination with other elements. The addition of phosphorus is widely used, increasing contact stability.

About half of all molybdenum-containing catalysts (45%) are contacts containing vanadium. They provide high conversion of acrolein to acrylic acid up to 80% and selectivity of the process up to 90%. Methacrylic acid yield in the oxidation of methacrolein is lower - up to 60%, selectivity 70-75%.

Additions of copper, antimony, tungsten, iron, tellurium, and bismuth considerably improve the properties of vanadium-molybdenum catalysts. On a complex V-Mo catalyst containing W and Cu and at least one of the metals: Sb, Fe, Ni, Co, Bi, acrolein is almost wholly oxidized into acrylic acid (96.3%), methacrylic acid yield-68.5%. Cobalt molybdates, often with additions of elements of V and VII groups of the periodic system, constitute a notable group among molybdenum-containing catalysts.

Active catalysts for the oxidative transformation of acrolein and methacrolein into acids are Mo-As-oxide systems with various additives, the best of which are nickel, palladium, and platinum. However, the substantial arsenic toxicity and high cost of noble metals make these catalysts unpromising for industrial application. Recently, preference is increasingly given to catalytic systems based on phosphorus molybdenum heteropoly acid with additives of ammonium ions, alkali metals, vanadium, tungsten, and antimony. The use of heteropolyacids (HPA) as oxidation catalysts seems promising because HPAs possess a unique set of valuable catalyst properties. They are polynuclear complexes of Mo^{VI} , W^{VI} and V^{V} that can also include many other elements as central atoms or ligands.

The intensity of new developments in the gas-phase catalytic oxidation of unsaturated C3-C4-aldehydes into the corresponding acids contributes to the design of catalytic systems with specific, pre-formulated properties. Such properties have at this stage of research phosphormolybdenum heteropoly acid with the addition of ammonium ions, alkali metals, vanadium, tungsten, and antimony as oxidation catalysts with the formation of the two-phase system of zinc molybdate and ammonium salt of heteropoly acid, as HPA are multi-electron oxidizers and simultaneously strong acids.

2. METHODS

HPAs are multi-electron oxidizing agents and simultaneously strong bronsted acids. Oxidation-reduction reactions and acidic properties of HPAs can be changed in a reasonably wide range by changing the composition of HPAs. This circumstance turns out to be extremely important because selective oxidation of unsaturated C3-C4-aldehydes into acids requires the presence of centers of optimal acid and oxidative strength on the catalyst surface. HPAs have a sufficiently high thermal stability in the solid-state. This creates an opportunity to use them as heterogeneous catalysts of oxidation reactions.

3. RESULTS AND DISCUSSION

Among various HPAs the acids and salts belonging to the saturated 12-row have the most significant importance for catalysis. They contain heteropolyanions (HPN) of the composition $\text{X}^{\text{x}} \text{M}_{12}^{\text{VI}} \text{O}_{40}^{\text{x}-8}$ or $\text{X}^{\text{x}} \text{M}_{12-n}^{\text{VI}} \text{V}^{\text{x}} \text{O}_{40}^{\text{x}-8}$. Representatives of series 12 are highly stable, and their properties have been sufficiently studied [3]. The HPA molecules of the 12th row of the indicated species have a Keggin structure with Td symmetry, which has been reliably established due to numerous X-ray studies of GPC crystal hydrates [3]. This structure includes a central tetrahedron XO_4 , surrounded by 12 octahedrons MO_6 , having common edges and vertices (O atoms).

X is the central atom (Si^{IV} , Ge^{IV} , P^{V} , As^{V} etc.);

x- degree of oxidation;

M- metal ion (Mo^{VI} , W^{VI})

The radius of HPA molecule $\sim 6\text{\AA}$ [4].

Since the ionic radius of O^{8-} significantly exceeds the radii of M^{VI} and X^{x} , the state of O in HPA is close to densely packed [3]. The HPA molecule contains the following types of chemical bonds: 12 quasilinear and 12 corners M-O-M bonds, four X-O-M bonds with bridging O atoms, and 12 M=O bonds with terminal O atoms. In these bonds, the coordination number of the oxygen atom is 2,2,4, and 1, respectively [3]. Thus, the HPA contains the main elements of the structure of Mo, W, and V oxides.

The most active and selective in the processes of oxidation of aldehydes into the corresponding acids were Mo HPAs Mo (P Mo_{12} , Si Mo_{12}). The results of research on cesium salts of different molybdenum heteropoly acids [5] showed that the systems based on cesium salt of phosphorus molybdenum heteropoly acid are the most effective in acid formation reaction. Cesium contributes to an increase in the yield of methacrylic acid, mainly due to an increase in selectivity. Introduction of additives of such

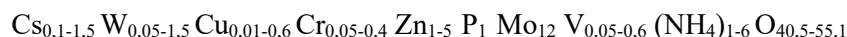
elements as V, W, Fe, Co, Ni, and Cr oxides, which turned out to be most active in the oxidation of methacrolein to acids, increase the activity of cesium salt of phosphonomolybdenum heteropoly acid.

In works [5, 6], the possibility was studied, and basic principles of modifying HPA-based catalysts by alkali metals were shown. It was shown that the catalytic properties of heteropoly compounds (HPC), namely the systems $M_x P M_{O12}$ (M-Li, Na, K, Cs; x=1,3,7) depend on the charge radius and coordination number of the introduced cation and its concentration.

It has been established that the presence of the Keggin cell [3] is a prerequisite for obtaining highly active systems based on phosphorus molybdenum acid salts. The activity and stability of the catalyst are related to the stabilization of the structure with wide channels in the volume of the HPC, occurring at the introduction of large radius cations. The real possibility of increasing the efficiency of catalysts based on HPC by varying the coordination number has been shown [6].

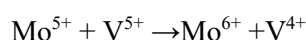
Taking into account other features of the introduced cation, it is possible to directionally change the catalytic properties of the HPA. Thus, the use of the features of the HPC structure, taking into account the nature, concentration, and properties of the introduced elements and modifying additives, opens up tremendous possibilities for the design of heterogeneous catalysts of given compositions with given properties. This is a new, promising, but still little studied direction in heterogeneous catalysis.

Studies in this area will undoubtedly be of interest not only for the theory of catalysis but also of great practical importance for increasing the efficiency of catalytic processes of organic synthesis. Firstly, processes of gas-phase catalytic oxidation of unsaturated aldehydes into corresponding acids. Having justified the choice of heteropolyacids and, in particular, phosphormolybdenum acids as good catalytic systems for the oxidative conversion of unsaturated C₃-C₄- aldehydes into corresponding acids, the introduction of various modified additives is of interest [2]. Such an approach to the study of phosphormolybdenum catalytic systems will significantly affect the structure and, consequently, the properties of heteropolyacids. The way of their preparation also plays an important role. We synthesized catalysts by two methods: a) based on ammonium salts of P and Mo) from phosphormolybdenum acid. In each series, the composition of the samples varied in a wide range and corresponded to the general formula:



A characteristic of both series of catalysts is the need for their activation. In the first hours of operation, the catalyst has low activity (degree of conversion of aldehyde <30%), which increases more than 3 times in steady-state mode. Steady-state mode is reached for a long time (35-40 h at 310°C), decreasing with increasing activation temperature (1-2 h at 360°C).

The activity of samples in each series weakly depends on the composition of synthesized catalysts. For polycomponent systems, it is complicated to estimate the contribution of one or another component or modifying additive to the activity and selectivity of the catalyst. Such an attempt was made for simpler catalysts synthesized from ammonium phosphate paramolybdate, ammonium vanadate, and zinc nitrate by precipitation from a standard aqueous solution and prepared based on phosphormolybdenum heteropoly acid [2]. It was shown that regardless of the preparation method, the catalysts are single-phase systems with the structure of the ammonium salt of phosphorus molybdenum acid. The introduction of vanadium does not affect the structure of the catalyst because V⁵⁺ ions, being a structural analog of Mo⁶⁺, can partially replace them in the lattice of the solid body with preservation of the structure. In this case, as shown [3], the rate of formation of selective oxidation products increases due to the acceleration of the oxidation-reduction processes of the catalyst due to charge transfer:



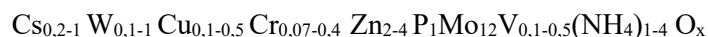
The addition of zinc in small amounts (Zn₁) has no effect on the selectivity of the catalyst concerning the target reaction; only the phase of the ammonium salt of Zn is found in the structure of the sample, and the amount of zinc molybdate phase is insignificant. With increasing the additive concentration

(Zn₂, Zn₃), the selectivity of transformation of methacrolein into methacrylic acid increases noticeably, further increasing Zn content in the catalyst (Zn₃). However, it reduces its activity and selectivity.

The formation and presence of a two-phase system consisting of zinc molybdate ZnMoO₄ and ammonium salt of heteropoly acid is the decisive condition for increasing the activity of multicomponent catalyst when zinc is introduced into its composition. The electron paramagnetic resonance (EPR) study of the catalyst formation from ammonium paramolybdate, ammonium phosphate, ammonium vanadate, and zinc nitrate (1 series) led to the conclusion that the formation of Keggin cells occurs at the stage of sample thermal treatment- vanadium ions compete with molybdenum ions for positions in the ammonium sublattice. These processes become more complicated in the presence of Zn ions. A zinc molybdate precipitate is formed during synthesis, and some vanadium ions are captured by this structure. Then, when the sample is heated, the ammonium salt of phosphate and ammonium ions, initially in solution, gradually forms. During this slow growth, more regular and larger crystals of the heteropoly compound are formed. The activating effect of zinc molybdate, which is not an oxidation catalyst, is that its crystals serve as a matrix on which the HPC is formed. In addition, a two-phase system is stabilized in the finished catalyst, which provides an increase in its activity. The second series of catalysts prepared based on phosphormolybdenum acid are single-phase systems without zinc molybdate. As known [2], the central structural unit of phosphormolybdenum heteropoly acid catalyst is Keggin cell. The introduction of alkali metal ions of equal radius changes the way of Keggin cell packing. The introduction of Cs contributes to some simplification of the Mo=O bond.

The properties and structure of HPCs strongly depend on the number of water molecules in the outer coordination sphere of the heteropolyanion (HPN) and cations and the channels between the individual HPNs. When samples are calcined to 300-380 °C, most of the water is removed, and the structure of dehydrated samples becomes dependent on the radius of the introduced cation. Naturally, the presence of large radius cations, including Cs, allows largely preserving the "openwork" porous structure even with almost complete dehydration [4]. It was found [1] that the initial activity and selectivity of phosphorus molybdenum catalysts increase when they are modified with alkali metals. The maximum effect is observed when Cs are introduced. Such catalysts appear to be particularly resistant to deactivation during operation. The stability of modified samples increases with the increasing radius of alkali metal. We determined the optimal concentration of Cs ions: 1<x<3. At x>3 the selectivity decreases sharply, and at x=7 the activity decreases.

Tungsten is an oxygen-containing element; tungsten ions in the composition of the catalyst increase its surface acidity and, consequently, its oxidative activity. Chromium and copper salts of phosphormolybdenum heteropoly acid also contribute to the activity and selectivity of the samples [2]. The results of tests of the synthesized phosphorus molybdenum-based heteropoly acid catalysts of both series (differing in the method of preparation) with a wide variety of sample compositions during gas-phase oxidation of methacrolein and methacrylic acid allowed to establish the optimal ratios of catalyst components and clarify its general empirical formula:



4. CONCLUSION

The developed catalyst of this composition provides a sufficiently high yield of the target product, in our case, during the oxidation of acrolein and methacrolein into the corresponding acids.

REFERENCES

- [1] Grimalyuk B. Oxidation of methacrolein in the gas phase on heterogeneous catalysts. Diss. Candidate of Chemical Sciences Lvov 1989; 148s.
- [2] Staroverova I., Kuttyrev M., Khvtistashvili L. Kinetics and catalysis vol. 27, no. Z.M., 1986 C; 691-697.

- [3] Huseynova E., Mamedova Z., Mustafayeva R., Analysis of experimental studies in the development of the theoretical foundations of the process of isobutene oxidation on oxide catalysts Oil refining and petrochemistry, No. 4, Moscow, 2016.
- [4] Guliyeva A., Huseynova E., Salakhova Y., Mustafayeva R., Mamedova Z. Modification and study by the planning method of the experiment of tin-antimony oxidation of isobutylene to methylacrolein, Natural and mathematical sciences in the modern world. Collection of articles of the XXVII International Scientific and Practical Conference Novosibirsk, 2015.